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# (12) UK Patent Application (19) GB (11) 2 120 666 A

(21) Application No 8312493  
 (22) Date of filing 6 May 1983  
 (30) Priority data  
 (31) 8215532  
 (32) 27 May 1982  
 (33) United Kingdom (GB)  
 (43) Application published  
 7 Dec 1983  
 (51) INT CL<sup>3</sup>  
 C07C 85/12 87/28  
 (52) Domestic classification  
 C2C 220 227 22Y 29X  
 29Y 311 31Y 321 326 32Y  
 360 361 36Y 43X 451  
 45Y 509 620 623 62Y 630  
 650 652 666 697 778 AA  
 LJ NB NN  
 U1S 1308 1347 C2C  
 (56) Documents cited  
 None  
 (58) Field of search  
 C2C  
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## (54) Hydrogenation process

(57) Hydrogenation of perhalogenated terephthalonitriles to their corresponding amines under acid conditions is suitably conducted under a pressure of 1 to 100 atmospheres and at a temperature of from 0 to 200°C in the presence of (i) a hydrogenation catalyst containing 0.1 to 70% by weight of a metal in Group 8 of the Periodic Table, (ii) an inorganic acid in an amount at least

chemically equivalent to the amine formed and (iii) a solvent which is inert to the reaction ingredients and which does not poison the catalyst; the concentration of nitrile in the total reaction mixture being from 3 to 25% by weight. Preferably water is present in the proportion of water to solvent from 1:50 to 1:1 parts by weight. The diamines obtained by this process are useful intermediates in the preparation of pesticidal compounds. 2,3,5,6-Tetrafluoroxylene diamine and its salts are novel compounds.

GB 2 120 666 A

The chemical formulae appearing in the printed specification were submitted after the date of filing, the formulae originally submitted being incapable of being satisfactorily reproduced.

# SPECIFICATION

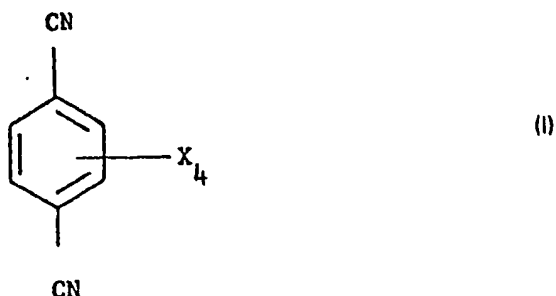
## Hydrogenation process

This invention relates to a process for hydrogenating perhalogenated terephthalonitriles and to novel compounds which can be obtained therefrom.

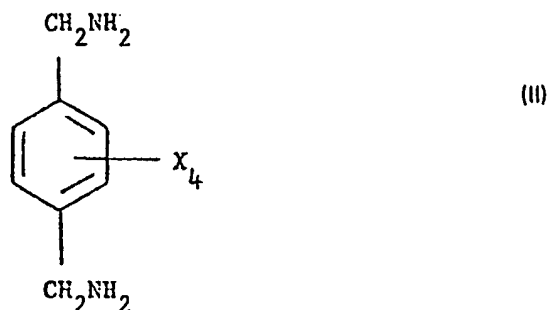
Processes for the hydrogenation of terephthalonitrile have been numerously described and as seen from, for example, UK Patent Specifications Nos. 810530, 852972 and 1149251, the hydrogenation is normally carried out under ammoniacal conditions.

Such conditions are not altogether suitable, however, for the hydrogenation of certain halo-substituted terephthalonitriles. For instance, in the case of tetrafluoroterephthalonitrile a high molecular weight material is produced thought to be the result of nucleophilic substitution of ring fluorine atoms by an amine group of the bifunctional hydrogenation product.

According to the present invention there is provided a process for hydrogenating a perhalogenated terephthalonitrile of the formula (I):



in which each X is independently fluoro or chloro, to its corresponding amine of formula (II):



which comprises reacting the terephthalonitrile with hydrogen in the presence of a hydrogenation catalyst under acid conditions.

The diamines obtained by this process are useful intermediates in the preparation of pesticidal compounds. 2,3,5,6-Tetrafluoroxylene diamine and salts thereof are novel compounds and form another aspect of the present invention.

Any suitable hydrogenation catalyst may be used. Generally, it will be a metal, particularly a metal in Group 8 of the Periodic Table, and will normally include rhodium, palladium, ruthenium, nickel, cobalt, platinum or copper as a component. The metal will usually be present upon a support such as carbon, alumina, alumina-silica, silica, kieselguhr, calcium carbonate, barium sulfate or bentonite. The active metal will usually be present in a proportion of from about 0.1 to 70% by weight, and, in the case of noble metals, generally 1 to 20%. A preferred catalyst is palladium preferably supported on charcoal and especially 5% palladium on charcoal. Nickel and cobalt catalysts, which tend to dissolve in acid conditions, may be less suitable.

The proportions of catalyst to nitrile may be wide-ranging. However, an amount of 0.5 to 5% by weight on nitrile has been found adequate for a catalyst containing a Group 8 noble metal.

The acid used to create the acid conditions is suitable an inorganic acid, particularly an oxyacid and ideally sulphuric acid, although other strong acids, such as hydrochloric acid, may also be suitable. At least an amount of acid chemically equivalent to the amine formed, should be used and preferably an excess up to, for instance, five times the chemically equivalent amount.

It may be prudent to add the acid continuously or intermittently during the process in case too high an acid concentration at the start of reaction, particularly when working at high nitrile concentrations, should have a deleterious effect on product yield.

It is expedient to slurry the barely soluble nitrile, together with all or part of the acid, in a solvent, preferably with water added. The solvent should be one that is inert to the reaction ingredients and does not poison the catalyst. Its choice will be influenced by operational consideration, the solubility in it of the reactant and intermediate and final products and obviously its effect on yield. Particularly suitable solvents are alcohols, especially aliphatic monohydric alcohols of the formula ROH, in which R is C<sub>1-6</sub> alkyl, and more especially methanol and ethanol. The presence of water gives processing advantages with respect to yield and an ability to operate at lower temperatures and pressures. 5

For ease of operation, it is desirable to have sufficient solvent and/or water present to provide a stirrable nitrile slurry. Suitably, the concentration of nitrile in the total reaction mixture will be from 3 to 15% by weight and even up to 25% by weight, particularly if the acid is added continuously or intermittently during the process. The proportion of water to solvent is usefully in the range of from 1:50 to 1:1 parts by weight. 10

The pressure and temperature of hydrogenation may vary within wide limits and will be chosen to suit the hydrogenation equipment available and to avoid too slow a reaction. Suitable pressures of from 15 1 to 100 or more atmospheres, conveniently from 1 to 30 atmospheres may be used at temperatures ranging from, for example, 0°C to 200°C and typically from 10°C to 120°C. Care must be exercised in working at higher temperatures to avoid dehalogenation of the product. For instance, prolonged processing at 150°C can lead to defluorination of tetrafluoroxylene diamine. 15

In carrying out the process of the invention, the nitrile starting material is conveniently charged to a glass lined or stainless steel rotary or stirred autoclave and slurried with all or part of the acid in the solvent and water. The autoclave is pressurised to the desired extent with hydrogen and rotated or stirred at the desired temperature until sufficient hydrogen has been absorbed. 20

The amine hydrogenation product is obtained as a salt which, in the solid phase, may be recrystallised from a water/solvent mixture and isolated by conventional techniques. The amine may be obtained in its pure form by solvent extraction techniques from a strongly alkaline solution of its salt. 25

Tetrachloroterephthalonitrile may be obtained from commercially available tetrachloroterephthaloyl chloride by treatment of the latter with aqueous ammonia to form the diamine which can then be dehydrated with, for example, phosphorus oxychloride. Other starting materials may be obtained by replacement with fluoro of one or more of the chloro substituents of the tetrachloroterephthalonitrile. Thus, tetrafluoroterephthalonitrile may be obtained by fluorinating the 30 corresponding tetrachlorinated compound with potassium fluoride in a polar aprotic solvent.

The invention is illustrated by the following Examples 1 to 30 in which percentages are by weight. Percentage yields of diamine are molar; yields of byproducts are computed from GLC traces assuming the same molar response factors as for the diamine. In all Examples, save Example 7 (q.v.), conversion of the dinitrile starting material was 100%. Example 31 is included for comparative purposes only. 35

#### EXAMPLE 1

Tetrafluoroterephthalonitrile (5.0 g), methanol (70 ml), water (2 ml), 98% sulphuric acid (3 g) and 5% palladium on carbon catalyst (0.25 g) were loaded into the glass liner of a rotating autoclave, purged with nitrogen, and then pressurised with hydrogen to 15 atmospheres. The autoclave was rotated for 6 40 hours at 75°C. The resulting slurry was filtered and the residue slurried with water. The aqueous solution was filtered to remove catalyst, then the water removed by heat until a crust formed on the liquid surface. 74 OP Ethanol was added to give 5.06 g of a white solid precipitate. This was dissolved in 5N sodium hydroxide and extracted repeatedly with ether. The residue after evaporation of the ether was recrystallised from toluene to give pure 2,3,5,6-tetrafluoroxylene diamine (m.pt. 89°C)

I.R. (KBr) 3385, 3275, 2955, 1600, 1480, 1348, 1268, 1165, 987, 928, 878, 828, 700 cm<sup>-1</sup>. 45

#### Proton nmr

2.09δ and 3.78δ, consistent with (2p, s, —NH<sub>2</sub>) and (2p, s, Ar—CH<sub>2</sub>—N) respectively.

UV (0.5N HCl in 50/50 methanol/water) 50  
λ<sub>max</sub> = 273 nm  
ε = 1.93 × 10<sup>3</sup>  
λ<sub>min</sub> = 234 nm

#### Elemental Analysis

	C	H	N	F
Found (%)	46.5	4.0	13.6	37.1
Calculated (%) (as C <sub>6</sub> H <sub>8</sub> F <sub>4</sub> )	46.1	3.9	13.5	36.5

55

**EXAMPLE 2**

Tetrafluoroterephthalonitrile (5 g), methanol (70 ml), water (10 ml), 98% sulphuric acid (3.5 g) and 5% palladium on carbon catalyst (0.25 g) were loaded into the glass liner of a rotating autoclave, purged with nitrogen, then pressurised with hydrogen to 30 atmospheres. The autoclave was rotated for 5 hours, during which time the temperature rose from 15°C to 18°C, and the pressure declined to 28 atmospheres. A slurry of catalyst and solid 2,3,5,6-tetrafluoroxyllylene diamine sulphate was filtered. The methanol was removed from the filtrate by reduced pressure distillation, and the aqueous residue, together with additional water, used to completely dissolve the separated solid sulphate product. 5 ml of this aqueous solution was added to 25 ml 10N sodium hydroxide solution, and extracted with four 10 ml aliquots of diethyl ether. GLC analysis of the combined aliquots showed the yield of 2,3,5,6-tetrafluoroxyllylene diamine to be 94.0% with 0.3% 4-cyano-2,3,5-tetrafluorobenzylamine, and no 4-aminomethyl-2,3,5-tetrafluoro-benzylalcohol or 2,3,5,6-tetrafluorobenzylamine.

**EXAMPLES 3 TO 6**

Further tetrafluoroterephthalonitrile reductions were carried out according to Example 2, but with the autoclave charges and reaction conditions summarised in Table I. It is to be noted that the higher pressure used favoured higher diamine yields.

TABLE I  
Hydrogenation of tetrafluoroterephthalonitrile in rotating autoclave

Example No.	REACTOR CHARGE					CONDITIONS			YIELDS			
	Nitrile g.	Methanol ml.	Water ml.	H <sub>2</sub> SO <sub>4</sub> g.	Cat. g.	Temp. °C	Press. at.	Time hrs.	DA	CA	AA	BA
3	15	70	20	9.0	0.2	12—15	30—20	6	87.4	0	2.0	0.9
4	10	70	10	6.0	0.125	12	30—25	6	86.3	0.8		1.8
5	5	70	10	3.5	0.125	14	7—5	6	81.5	1.1	4.5	3.8
6	5	70	10	3.5	0.25	12—19	7—4	7	75.2	0.3	12.6	2.6
7	10	40	40	6	0.125	10	30—20	6	96.0*	0	0	0

DA = 2,3,5,6-tetrafluoroxylene diamine

CA = 4-cyano-2,3,5,6-tetrafluorobenzylamine

AA = 4-aminomethyl-2,3,5,6-tetrafluorobenzyl alcohol

BA = 2,3,5,6-tetrafluorobenzylamine

\* conversion 61%

**EXAMPLE 8**

Tetrafluoroterephthalonitrile (30 g), methanol (420 ml), water (90 ml), 98% sulphuric acid (21 g) and 5% palladium on carbon catalyst (1.5 g) were loaded to a 1 litre 316 stainless steel autoclave, fitted with a glandless agitator and gas recirculation facility. The autoclave was purged with nitrogen and the contents maintained under 30 atmospheres of hydrogen pressure while agitation was continued for 6 hours. During this time the temperature rose from 20°C to 28°C. The product slurry was treated and analysed as in Example 2. The yield of 2,3,5,6-tetrafluoroxylene diamine was 91%, with 0.3% of 2,3,5,6-tetrafluorobenzylamine.

**EXAMPLES 9 TO 13**

Further tetrafluoroterephthalonitrile reductions were carried out according to Example 8, but with the autoclave charges and reaction conditions summarised in Table IIK. Again, the higher pressures gave superior diamine yields.

TABLE II  
Hydrogenation of tetrafluoroterephthalonitrile in stirred autoclave

Example No.	REACTOR CHARGE					CONDITIONS			YIELDS			
	Nitrile g.	Methanol ml.	Water ml.	H <sub>2</sub> SO <sub>4</sub> g.	Cat. g.	Temp. °C	Press. at.	Time hrs.	DA	CA	AA	BA
9	30	420	90	21	1.5	5—15	32	6	88	0	0	0.04
10	10	280	20	7	0.25	17—15	7	6	86	0	1.0	4
11	20	420	60	14	1.0	20—18	30	6	83.3	0.1	1.9	0.4
12	10	280	20	7	0.25	15—18	3.5	6	75	0.3	1.6	0.8
13	20	280	20	11	0.5	20—15	28	6	65	3.8	3.0	8.4

**EXAMPLE 14**

Tetrafluoroterephthalonitrile (5 g), methanol (70 ml), 98% sulphuric acid (3.5 g) and 5% palladium on carbon catalyst (0.125 g) were vigorously agitated under hydrogen at atmospheric pressure for 4.25 hours at 20°C. The resulting slurry was filtered, water added to the filtrate and the methanol removed by reduced pressure distillation. The sulphates in the residue from the hydrogenation were dissolved in the resulting aqueous solution. The products of the hydrogenation were assessed by the procedure described in Example 2. Yields were 27.4% 2,3,5,6-tetrafluoroxylenylenediamine, 7.6% 4-cyano-2,3,5,6-tetrafluorobenzylamine and 9.2% 2,3,5,6-tetrafluorobenzylamine.

**EXAMPLES 15 TO 25**

Further tetrafluoroterephthalonitrile hydrogenations were carried out according to Example 14, but with varying catalyst and acid additions, and in some Examples, water addition. Results are described in Table III. Water is seen to enhance markedly the diamine yield.



TABLE III  
Hydrogenation of tetrafluoroterephthalonitrile at atmospheric pressure

Example No.	REACTOR CHARGE					CONDITIONS		YIELDS			
	Nitrile g.	Methanol ml.	Water ml.	H <sub>2</sub> SO <sub>4</sub> g.	Cat. g.	Temp. °C.	Time hrs.	DA	CA	AA	BA
15	5	70	0	3.5	0.06	20	7.0	19.8	14.5	0	11.9
16	5	70	0	3.5	0.5	20	16.5	18	0	2.6	2.0
17	5	70	0	3.5	0.06	55	6	15.5	2.4	0	
18	5	70	5	3.0	0.25	20	3	65	4.8	1.1	13.7
19	5	70	5	3.5	0.125	17		53	3	0.6	17.0
20	5	70	10	2.75	0.25	20	4.5	49	6.5	0.7	14.1
21	5	70	10	3.0	0.25	20	2.25	60	1.0	11.7	3.6
22	5	70	10	3.0	0.125	19	4	49	10.5	0	14.4
23	5	70	10	3.5	0.125	20	4	50	1.4	4.0	19.6
24	5	70	10	4.0	0.125	20	4	50	0.4	10.0	14.4
25	5	70	10	5.0	0.125	20	4	38.3	0	6.7	25.2

## EXAMPLES 26, 27 and 28

Tetrafluoroterephthalonitrile (2.5 g), methanol (70 ml) and 5% palladium on carbon catalyst (0.125 g) were loaded to the glass liner of a rotating autoclave, together with 98% sulphuric acid and water in the amounts indicated in Table IV. After purging with nitrogen, the autoclave was pressurised to 10 atmospheres with hydrogen, rotated and heated for the time shown in Table IV. The product suspension was filtered, and the residue and filtrate quantitatively analysed for 2,3,5,6-tetrafluoroxyllylene diamine by high pressure liquid chromatography.

If Examples 26 and 27 were carried out at 75°C, it could be expected that the UV spectrum of the solution phase would indicate the presence of 4-cyano-2,3,5,6-tetrafluorobenzylamine ( $\lambda_{\text{max}} = 234$  nm in 0.5 N HCl).

Examples 26 to 28 illustrate the beneficial effect of water and the better yield obtained when using a higher acid : nitrile molar ratio.

TABLE IV

Example No.	H <sub>2</sub> SO <sub>4</sub> :nitrile (molar ratio)	Water ml.	Temp. °C.	Time hrs.	% Yield diamine		
					Solution	Solid	Total
26	1.6:1	0	90	3	48	35.3	83.3
27	1.2:1	0	92	6	10	46	56
28	1.2:1	2	75	6	8	64.1	72.1

## EXAMPLE 29

Tetrafluoroterephthalonitrile (10 g), 74 OP ethanol (70 ml), water (5 ml), 98% sulphuric acid (6.4 g) and 5% palladium on charcoal catalyst (0.5 g) were charged to the glass liner of a rotating autoclave and pressurised to 15 atmospheres with hydrogen. The autoclave was rotated at 60°C for 6 hours. The resulting slurry was filtered; high pressure liquid chromatography showed the 2,3,5,6-tetrafluoroxyllylene diamine yield to be 72.2% and all in the solid residue.

## EXAMPLE 30

Tetrafluoroterephthalonitrile (2.5 g) 5% palladium on charcoal catalyst (0.125 g), sulphuric acid (6.4 g) and methanol (70 ml) were charged to a glass lined rotary autoclave. The autoclave was pressurised to 50 atmospheres with hydrogen, and rotated for 4 hours at 110°C. The resulting slurry was cooled, filtered and the solid phase recrystallised from a mixture of water and methanol. Elemental analysis, fluorine nmr, proton nmr, infra red and mass spectra (the latter after the sample was heated with sodium bicarbonate), were consistent with the recrystallised material being tetrafluoroxyllylene diamine sulphate.

The material gave a single peak on a high pressure liquid chromatogram, when using a mixed ion pair/electrolyte elution system.

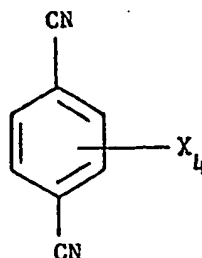
## EXAMPLE 31

This example is included for comparative purposes only.

Tetrafluoroterephthalonitrile (2.5 g), nickel catalyst (Harshaw 5132P) (0.8 g), methanol (70 ml) and ammonia (12 g) were charged to a glass lined rotating autoclave. After pressurising to 30 atmospheres with hydrogen, the autoclave was rotated at 110°C for 3 hours. After cooling, filtering off the catalyst, and removing residual ammonia and methanol by distillation, a brown solid remained. Infra red spectroscopy indicated this to be a high molecular weight material, with some loss of ring fluorine, and the presence of an amine hydrohalide.

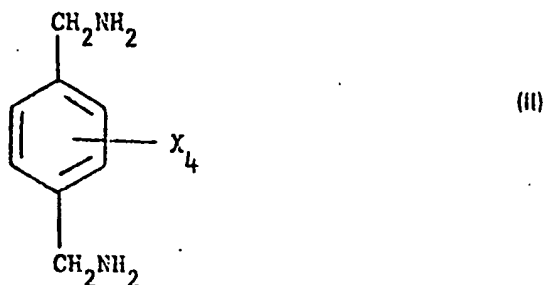
## CLAIMS

1. A process for hydrogenating a perhalogenated terephthalonitrile of the formula (I):



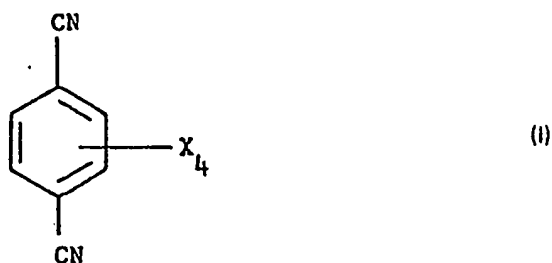
(I) 40

In which each X is independently fluoro or chloro, to its corresponding amine of formula (II):

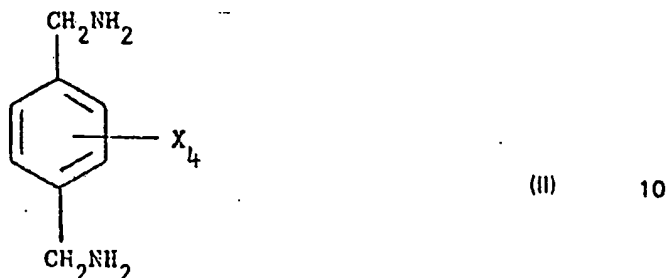


which comprises reacting the terephthalonitrile with hydrogen in the presence of a hydrogenation catalyst under acid conditions.

- 5      2. A process according to claim 1 for hydrogenating tetrafluoroterephthalonitrile to form 2,3,5,6-tetrafluoroxylene diamine.      5
3. A process for hydrogenating a perhalogenated terephthalonitrile of the formula (I):



In which each X is independently fluoro or chloro, to its corresponding amine of formula (II):



- 10      which comprises reacting the terephthalonitrile with hydrogen under a pressure of 1 to 100 atmospheres and at a temperature of from 0 to 200°C in the presence of (i) a hydrogenation catalyst containing 0.1 to 70% by weight of a metal in Group 8 of the Periodic Table, (ii) an inorganic acid in an amount at least chemically equivalent to the amine formed and (iii) a solvent which is inert to the reaction ingredients and which does not poison the catalyst; the concentration of nitrile in the total reaction mixture being from 3 to 25% by weight.      15

4. A process according to claim 3 in which water is present in such amount that the proportion of water to solvent is from 1:50 to 1:1 parts by weight.
5. A process according to claim 3 or 4 in which the catalyst contains from 1 to 20% by weight of a metal selected from rhodium, palladium, ruthenium and platinum.      20
6. A process according to any one of claims 3 to 5 in which the solvent is an alcohol.
7. A process according to any one of claim 3 to 6 in which the pressure is from 1 to 30 atmospheres.
8. A process according to any one of claims 3 to 7 in which the temperature is from 10 to 120°C.
- 25      9. A process for hydrogenating tetrafluoroterephthalonitrile to form 2,3,5,6-tetrafluoroxylene diamine substantially as described with reference to any one of Examples 1 to 29.      25
10. 2,3,5,6-Tetrafluoroxylene diamine and salts thereof.

DERWENT-ACC-NO: 1993-259435

DERWENT-WEEK: 199333

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TITLE: Olefin prodn. used for mfr. of polymers and  
surfactants  
- comprises selective catalytic hydrogenation  
of cyclic,  
acrylic linear or branched diene(s) over  
activated  
palladium salt catalyst system in simple  
process at low  
temp. and pressure

INVENTOR: BEHR, A; SCHMIDKE, H

PATENT-ASSIGNEE: HENKEL KGAA[HENK]

PRIORITY-DATA: 1992DE-4203351 (February 6, 1992)

PATENT-FAMILY:

PUB-NO	PUB-DATE	LANGUAGE
PAGES MAIN-IPC		
DE 4203351 A1	August 12, 1993	N/A
006 C07C 005/05		

APPLICATION-DATA:

PUB-NO	APPL-DESCRIPTOR	APPL-NO
APPL-DATE		
DE 4203351A1	N/A	1992DE-4203351
February 6, 1992		

INT-CL (IPC): B01J023/44, C07C005/05 , C07C011/02 , C07C011/107 ,  
C07C013/36

ABSTRACTED-PUB-NO: DE 4203351A

BASIC-ABSTRACT:

Prodn. comprises hydrogenating linear or branched, cyclic or open-  
chain dienes  
(II) with H<sub>2</sub> at 0-150 deg.C and 800-1500 hPa in the presence of a  
catalyst  
system (III) contg. a Pd salt (IV), an activator (V), opt. a base  
(VI) to  
neutralise the acid formed on redn. of (IV) and/or water and/or an

inert,  
water-immiscible solvent (VII).

Pref. (II) are 4-20C dienes. (IV) is pref. a Pd(II) (pseudo)halide, acetate and/or acetylacetonate. (V) is pref. DMF, DMA, NMP, acetonitrile and/or tetramethylurea; or a mono- or di-(1-4C)alkyl carbonate of the formula  $R_1-O-CO-O-R_2$  (VA) and/or a cyclic carbonate of formula (VB) where  $R_1$  and  $R_2$  are H or 1-4C alkyl. The pref. molar ratios are (IV):(II) is 1:(5-20000) and (IV):(V) is at least 1:10. The pref. reaction temp. is 10-60 deg.C.

USE/ADVANTAGE - (I) are widely used in the chemical industry, e.g. for producing polymers and surfactants. Hydrogenation of (II) to (I) is selective and avoids formation of completely satd. prods.. The process is simple and operates at relatively low temps. and pressures. (III) is resistant to many catalyst poisons, allowing (II) of variable quality to be hydrogenated.

In an example, a soln. of 5g (0.061 mole) cis-1,4-hexadiene in 5g DMA was treated with a colloidal Pd catalyst, prep'd. by in-situ redn. of 4.17mg  $PdCl_2$  with  $H_2$  in the presence of 2.8mg NaCl and 13.5mg hydrated  $Na_2CO_3$  crystals. Hydrogenation was carried out at 25 deg.C, with intensive stirring, using the calculated amt. of  $H_2$ , which was taken up completely in 90 mins.. The prod. contained 86.1 (wt.)% hexene isomers, 1.1% hexane and 12.8% hexadiene isomers.

CHOSEN-DRAWING: Dwg.0/0

TITLE-TERMS: OLEFIN PRODUCE MANUFACTURE POLYMER SURFACTANT COMPRISE  
SELECT

CATALYST HYDROGENATION CYCLIC ACRYLIC LINEAR BRANCH DIENE  
ACTIVATE  
PALLADIUM SALT CATALYST SYSTEM SIMPLE PROCESS LOW  
TEMPERATURE  
PRESSURE

DERWENT-CLASS: A41 E17

CPI-CODES: A01-D13; E10-J02C3; N02-F;

CHEMICAL-CODES:

Chemical Indexing M3 \*01\*

Fragmentation Code

H7 H721 M210 M214 M215 M216 M220 M221 M222 M223  
M224 M225 M226 M231 M232 M233 M320 M416 M610 M720  
M903 M904 N213 N309 N321 N412 N441 N442 N511 N512  
N513 N522 Q110

Specific Compounds

02043P 03187P 22179P

Markush Compounds

199333-A2701-P

Chemical Indexing M3 \*02\*

Fragmentation Code

G000 G050 G552 G582 M280 M320 M415 M510 M520 M530  
M541 M610 M720 M903 M904 N213 N309 N321 N412 N441  
N442 N511 N512 N513 N522 Q110

Specific Compounds

01140P 01469P

Markush Compounds

199333-A2702-P

Chemical Indexing M3 \*03\*

Fragmentation Code

A546 A940 A960 C000 C017 C100 C710 C730 M411 M730  
M903 Q421

Chemical Indexing M3 \*04\*

Fragmentation Code

M413 M416 M730 M903 Q422

UNLINKED-DERWENT-REGISTRY-NUMBERS: 0247S; 0278S ; 0342S ; 1047S ;  
1140P ; 1402S  
; 1469P ; 1532S ; 1705S ; 2043P

ENHANCED-POLYMER-INDEXING:

Polymer Index [1.1]

017 ; G0033\*R G0022 D01 D02 D51 D53 D84 D85 D86 D87 D88 D89 D90  
D91 D92 D93 D94 ; R02043 G0044 G0033 G0022 D01 D02 D12 D10 D51  
D53

D58 D86 ; H0271 ; L9999 L2471 ; L9999 L2722 L2711

Polymer Index [1.2]

017 ; ND02 ; ND03 ; K9654 ; K9665

Polymer Index [1.3]

017 ; D00 D01 D11 D10 D50 D61\*R D70 F23 7A\*R Pd 8B Tr ; R05294  
D01

D11 D10 D50 D61 D84 F36 F35 Pd 8B Tr ; C999 C102 C000 ; C999 C259

Polymer Index [1.4]

017 ; D01 D11 D10 D50 D84 F78 D63 D82 D83 D85 D86 D87 D88 F44 D89  
D90 ; R00278 D01 D11 D10 D50 D83 F70 ; R00342 D01 D11 D10 D50 D82  
F12 ; R01084 D01 D11 D10 D50 D84 F70 ; R05268 D01 D11 D10 D23 D22  
D31 D41 D50 D85 F71 ; C999 C124 C113

POLYMER-MULTIPUNCH-CODES-AND-KEY-SERIALS:

- Key Serials: 0034 0036 0037 0106 0109 0112 0115 0118 0121 0124 0127  
0130 0214  
0227 0229 0237 0295 2038 2043 2044 2051 2065 2189 2204  
Multipunch Codes: 017 02- 03- 041 046 054 07- 075 09& 09- 10& 10- 15&  
17& 17-  
18& 18- 19& 248 263 273 278 293 343 351 360 681 689 693 726

SECONDARY-ACC-NO:

CPI Secondary Accession Numbers: C1993-115228